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PRESENT-DAY KNOWLEDGE OF THE CHEMICAL COMPOSITION OF COAL

BY

J. B. SHOHAN

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DEPARTMENT OF COMMERCE - BUREAU OF MINES

PRESENT-DAY KNOWLEDGE OF THE CHEMICAL CONSTITUTION OF COAL [a]

By J. B. Shohan[b]

Ordinary (bituminous) coal has been defined by Stopes and Wheeler[1] as "a compact, stratified mass of 'mummified' plants (which have in past suffered arrested decay to varying degrees of completeness), free from all save a very low percentage of other matter" like the plant products from which it originated. Coal is therefore a heterogeneous mass of several physically and chemically different classes of compounds, held together perhaps by some such loose chemical union as has been suggested for the constituents of wood.[2] The properties of various coals, as we know them, thus depend on the proportions in which these classes are present and on the nature of the individual substances which comprise them; the elucidation of the chemical constitution of coal depends on the knowledge of the structure of these different types of matter.

While at first sight this task appears to be hopeless, there can be little doubt that the results of coal research within the past decade have considerably lightened the burden. Indeed, R. V. Wheeler[3], one of the pioneers of modern coal research, optimistically has said: "The constitution of coal may seem a wide one; I have come to the conclusion that it is not as wide as is generally imagined. I wish, in fact, to argue the essential simplicity, chemically, of coal rather than its complexity." That such optimism is not universal among workers in this field may be gathered from a statement by another authority, Tropsch,[4] who said, "It is doubtful" (admitting the great advances made in recent years) "if the methods of classical organic chemistry can explain completely the constitution" of the actual coal substance. The widely differing points of view expressed in these statements are, however, merely due to the fact that while the one investigator looks back to the past and becomes encouraged by the recent important progress, the other sees despairingly the enormous strides that must be made in the future before the structure of coal will stand revealed. It is the purpose of the present paper to summarize briefly the present status of the constitution of coal from the chemist's standpoint, emphasizing especially the contributions made during the last five years.

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1 - Numbers refer to bibliography at end of this paper.

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CHEMICAL NATURE OF COAL

Evidence as to the chemical nature of coal has come from two sources:

I. Study of the coal substance as a whole, including (a) microscopic investigation, (b) decomposition by heat (carbonization and gasification), (c) spontaneous heating, (d) treatment with solvents, and (e) behavior towards reagents.

II. Examination of distinct constituents of coal, including (a) 1, the microscopically distinct or mechanically separable ingredients, vitrain, clarian, durain, and fusain; 2, anthraxylon, and attritus; 3, spore exines, cuticles; (b) the various fractions obtained by solvent extraction chiefly with pyridine, chloroform, benzene, petroleum ether, and phenol; and (c) the humic (or ulmic) portion regenerated from coal by oxidation or obtained direct from the younger brown coals.

In view of the vast output of published research in the fields enumerated, it is impossible to consider all the work fully. Fortunately, excellent comprehensive reviews of the work up to 1924 are available in both English[5] and German,[6] and these are substantially up-to-date so far as the topics of Group I are concerned. The reason for this is that coal chemists now realize that little can be gained by studying the behavior of the entire coal conglomerate, and that the more logical method of attack is upon isolated and different classes of compounds into which coal can be resolved by various means.[7] For the sake of completeness, however, a brief résumé of the extensive literature on the chemistry of the coal substance as a whole will be given.

I. STUDY OF COAL SUBSTANCE AS A WHOLE

(a) Microscopy of Coal. - The brilliant researches of a number of investigators in this field have thrown a great deal of light on the origin and constitution of coal, and have definitely linked the chemistry of coal with that of plants and their products of decomposition. The chemist is indebted to these investigators who have stimulated him and have supplied him with valuable information, but obviously it is beyond the power of the microscope to reveal the submicroscopic structure of matter in which the chemist is primarily interested.

Thanks to the microscopist the coal chemist has been forced to realize that the chemistry of plants, of their decay, and of intermediate products of coalification (for example, peat and brown coal) must receive his full share of attention if he would solve completely the chemistry of coal.[8]

(b) Decomposition of Coal by Heat. - In the absence of any more direct evidence, the behavior of coal on heating has been used to formulate certain theories regarding its constitution. Thus, it has been affirmed[9] that coal contains two classes of compounds differing in their decomposition temperature, the one yielding below 700° C. chiefly hydrocarbons, the other decomposing at a critical temperature near that point and giving hydrogen and oxides of carbon.

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Porter[10] states, however, that "this view as to a distinct characterization of classes of material present, by behavior in decomposition, has not been generally accepted and in fact has been modified[11] in a measure by the proponents." They admit that the apparent "critical" temperature at about 700° is probably not the decomposition temperature of an original component of coal, but of a residue from the treatment at lower temperatures.

As a result of further studies of the decomposition of coal by heat, Jones and Wheeler[12] proposed a theory of the chemical constitution of what they considered the two constitutents of coal: (1) The "cellulosic", consisting of (a) the alpha fraction insoluble in pyridine, and (b) the beta fraction soluble in pyridine and insoluble in chloroform; and (2) the "resinic" or gamma fraction soluble both in pyridine and in chloroform. Briefly, they postulated for the first group a furane structure which has a doubly unsaturated four carbon-oxygen ring system, and for the second the existence of "bound" molecules of the type $RH.C_nH_{2n+1}$ or $RH.C_nH_{2n-1}$ which decompose to give free hydrocarbons. The theory of these investigators was largely speculative and based chiefly on analogies drawn from the behavior of known compounds; therefore, the evidence advanced can not be considered sufficient or conclusive.

(c) Spontaneous Heating.[13] - The practical significance of the phenomenon of spontaneous combustion of coal in storage has led a number of investigators to study the problem. Although most of the work has been done from a practical point of view, there has also been a good deal of speculation on the fundamental properties of the coal substance which is responsible for this behavior on exposure to air. In fact, a great deal of the theoretical work on the constitution of coal, particularly in England, was undertaken to shed further light on this important subject (and the related problem of the explosibility of coal-dust), the chief aim being to determine which portion of the coal conglomerate was responsible for its "self-heating." Thus interest has been centered on the pyrite in coal[14] and on the oxidizable "ulmic" portion.[15] Of these, the latter is, for the purpose of this paper, by far the more important and will later be considered in detail.

(d) Treatment of Coal with Solvents.[14] - Numerous attempts have been made to separate the various constituents of coal by means of solvents. The chief value of these efforts has been, however, to call attention to the complex nature of coal and to the futility of studying it chemically in its entirety. Thus the "gamma" or"resinic" (pyridine and chloroform soluble) portion has entirely different properties from the remainder of the coal, and will be considered separately. Likewise, the pyridine and chloroform residue has been further resolved into different types of matter which have been studied by themselves. Of the other solvents, benzene at 200 to 300° C. under pressure has yielded both solid and oily "bitumens", but little is known concerning their chemical properties.

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(e) Behavior of Coal Towards Chemical Reagents.[15] - The use of reagents to determine the chemical constitution of coal goes back to Gay-Lussac one hundred years ago.[16] Nitric, sulphuric, iodic, chromic, chloric, and chlorsulphuric acids, water, sulphuryl chloride, potassium permanganate and other oxidizing agents, hydriodic acid and other reducing agents, hypochlorites, ozone, alkalies, halogens, and potassium hydride have all been tried by many workers. On the whole, it can not be said that the yield of information resulting from the enormous amount of work done is very high. The most useful reagents by far are the oxidizing agents, and these have been used to shed light not only on the constitution of coal but also on the origin. Fischer and Schrader[17] thus obtained as high as 10 per cent of aromatic acids, mellitic, mellophtalic, and isophtalic acids. They utilized their findings to substantiate their well-known theory that coal is essentially aromatic in nature, being derived from the supposedly aromatic component of wood--namely, lignin. Of great importance in the study of the chemistry of coal is the fact that on oxidation, certain portions of the coal conglomerate form alkali-soluble products. As the ulmins are the most important single constituent of coal, they are considered in detail in the following section.

II. Examination of the Distinct Constituents of Coal

(a) The Four Ingredients of Banded Bituminous Coal. - In 1919 Stopes[18] brought forward the idea that banded bituminous coal may be mechanically separated into four ingredients, as follows:

(1) Fusain - the equivalent of "mother of coal", "mineral charcoal," etc.

(2) Durain - the equivalent of "dull" hard coal of various authors; the "mattkohle" of the Germans.

(3) Clarain - banded bright luster

(4) Vitrain - conchoidal fracture brilliant in appearance

} Together the equivalent of "bright" or glanz coal of various authors; the "Glanzkohle" of the Germans.

This classification was generally accepted in England, and most of the subsequent work with coal carried on in that country started with those separate ingredients. The results obtained by these numerous investigators have shown that the differences between the last three groups "seem to be due to a variation in the proportions in which the constituents of the coal conglomerate are present in each ingredient of the banded coal, rather than to the presence in any one of them of fundamentally distinct types of compounds." In other words, the mechanical separation of coal did not yield any essentially different chemical types.[19]

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(b) The Anthraxylon and Attritus of Thiessen. - As a result of his extensive microscopic investigation of various coals, Thiessen[20] has concluded that the chief constituents of all bituminous coals may be divided into two classes: (1) Anthraxylon, which is found in bright bands and is derived from the woody tissues of plants; and (2) attritus, found in the duller portions and consisting of finely macerated plant mass or "attrition matter", derived from all kinds of products, together with more "highly fragmented anthraxylon."

This classification, like that of Stopes, is essentially physical and is important from the viewpoint of the student of the origin of coal and its physical relation to its mother substance. To the chemist, on the other hand, the problem of the constitution is first to separate the conglomerate into chemically different groups and then to identify members of each group.

(c) Tideswell and Wheeler's Views. - Tideswell and Wheeler[21] have, it seems, attempted to bring together Stopes' and Thiessen's views and state that "the various plant entities and residues that have contributed to the formation of the organic substance of coal can conveniently be grouped according as they are:

(1) Resistant to decay. - Among the more important members of this group are (a) spore exines and cuticular tissues; and (b) resins.

(2) Subject to decay. - Members of this group are (a) organized, such as cellulosic and lignified tissues; (b) amorphous, the contents of plant cells.

(3) The products of decay. - The ulmins: It is further postulated that 'as they finally appear in the coal, cell-wall structures, group 2 (a) may not differ much, chemically, from the amorphous ulmins, but the materials of group 1 differ markedly.' "

Wheeler[22] concludes from this that it is "to be expected that, chemically, coal will be divisible into two main groups of substances, differing considerably from each other; the one composed of the resistant plant materials, perhaps in a somewhat changed form, the other the ulmins derived from the less resistant cellular structures and cell contents."

This division may be open to attack on the grounds of its being simpler than the facts indicate, but there can be no doubt that Wheeler's conception of the essential simplicity of coal has given great impetus to the rational study of its chemical composition. Thus, in the last few years several important publications have appeared which deal with the constitution of the various chemically distinct components into which coal may be separated. These are (1) the hydrocarbons and resins; (2) the organized plant entities such as the cuticles; and (3) the ulmins.

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III. The Different Types of Organic Substances into which Coal May be Resolved

(a) The Resins. - The presence of small amounts of resin-like inclusions in bituminous coal has been demonstrated conclusively by several observers. Wigginton[23] examined chemically 13 samples derived from British and American coals and found that the resins were always richer in carbon and hydrogen than the coals from which they were derived. The average percentages found were carbon 81.7 and hydrogen 8.6. Organic solvents resolved the resins into various fractions, indicating that they are not homogeneous substances. Tests for resin acids gave negative results. Free hydrocarbons saturated or unsaturated were also found to be absent. Molecular-weight determinations gave a figure of approximately 1000, and acetylation showed the presence of 1 to 2 per cent of hydroxyl oxygen. Finally, thermal decomposition of two samples gave almost equal quantities (roughly 40 per cent each) of coke and tar and a gas rich in paraffin hydrocarbons and hydrogen, besides small quantities of unsaturated hydrocarbons.

By well-regulated oxidation of a Hampstead vitrain and subsequent treatment with alkali, Francis and Wheeler[24] obtained yellow rods which were doubtless resin inclusions. These were soluble in chloroform and on analysis showed 80.6 per cent carbon and 10.3 per cent hydrogen.

(b) The Bituminous Matter in Coal. - A larger and, from the point of view of industry, a more important group of substances are those which can be extracted from coal by means of various solvents. These are held to be derived from the oils, fats, waxes, and resins of the original coal-forming plant material. A large number of solvents have been used to extract these substances from coal, but actually pyridine, chloroform, and benzene have yielded the best results.

The Pyridine-Chloroform Soluble, So-Called Gamma, Portion of Coal. - Continuing the early work of Clark, Jones and Wheeler,[9c, 12a, d] Cochram and Wheeler[25] have investigated further the gamma portions of a large number of bituminous coals. The pyridine-chloroform soluble portion was further fractionated by extraction with light petroleum, ethyl ether, and acetone. The portions dissolved by each of these were called gamma-1, gamma-2, and gamma-3, respectively, while the residue was termed gamma-4. Table 1 summarizes the analytical results obtained.

Table 1. - Resolution of gamma compounds in Parkgate-A clarain

	Per cent of total gamma compounds	Per cent of coal	Ultimate analysis, per cent			
			C	H	S	O + N
Gamma 1	33	2.30	83.90	9.00	0.74	6.36
Gamma 2	37	2.54	82.72	6.90	0.91	9.47
Gamma 3	12	0.83	79.00	5.70	0.81	14.41
Gamma 4	18	1.23	80.00	5.90	1.10	13.00

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Further examination of the four fractions showed that they were constituted as follows:

Gamma 1. - A mixture of white crystalline compound with red oil. Contains oxygenated compounds consisting of traces of bases and fatty acids, resins, saturated and unsaturated hydrocarbons (analysis: C, 87.4; H, 11.3; O, 1.47 per cent).

Gamma 2. - Small quantities of acids and pyridine bases, some saponifiable material consisting chiefly of complex phenols, traces of an acid volatile with steam, hydroxy acids in the form of esters similar to the "resines" or "resinols" of Tschirch and nonsaponifiable matter similar to "resenes."

Gamma 3 and 4. - These constitute a dark-brown high-melting powder which differs markedly from the first two portions, and on account of their similar behavior they are grouped together.

The various gamma fractions were further studied by means of destructive distillation and regulated oxidation. Thus the former treatment showed that the gamma constituents consist mainly of hydrocarbons, resins, and a third group which has mixed properties of resins and coal-ulmins.

The Benzene-Pressure Extracts of Coal. - The extraction of coal with benzene under pressure at temperatures of 200 to 300° C. was first tried by Fischer and his associates.[23] They found the extract to consist of two portions; the one called "solid bitumens" is insoluble in light petroleum ether; the other called "oily bitumens" (consisting of hydrocarbons) is soluble in that solvent. In a very recent paper Davis and Reynolds[27] report a third product which is soluble in benzene under the conditions of extraction but precipitates from solution on cooling; this they call "insoluble bitumen." (If one may judge from the ultimate analyses reported, the two solid bitumens consist of similar types of compounds.) These investigators, as well as others, have in part attempted to correlate the properties of the benzene extracts with the important coking property of bituminous coals. At present there is considerable interest and controversy in this field, but with the exception of ultimate analyses and melting or decomposition temperatures, no fundamental data are obtainable on the chemical nature of the bitumens.

Comparison Between Pyridine-Chloroform and Benzene-Pressure Extracts. - Cockram and Wheeler[25] concluded from a resolution of their benzene-pressure extracts of Parkgate-A coal with ethyl ether and acetone that, on the whole, the gamma compounds and the mixed bitumens obtained from the benzene solutions were constituted alike; however, they note that this is not necessarily so for all coals. Further work along these lines seems to be highly desirable.

(c) The Organized Plant Entities of Coal: Plant cuticles. - Cuticles constitute the outer protective coverings of plant bodies. Their existence in bituminous coal is well established; in the unique Russian deposit of so-called paper-coal they represent 20 per cent of the total coal.

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In the course of their systematic attack on the constitution of coal, the Safety in Mines Research Board of Great Britain has been studying the chemistry of plant cuticles. For the purpose of developing a technique in handling the cuticles existing in coal which are accessible with difficulty, Legg and Wheeler[28] have been studying a typical modern plant cuticle--that of the Agave Americana. They obtained mainly four fractions: A water-soluble material, wax, cellulose, and most abundant of all, a residue called "cutin," which is said to be derived from the oxidation of unsaturated constituents of fats and waxes with which it is associated. From the latter have been derived two acids, cutic and cutinic, having the empirical formulas $C_{36}H_{50}O_6$ and $C_{15}H_{22}O_6$. Furthermore, on distillation cutin yields 60 per cent of tarry products from which pentatriacontane, $C_{35}H_{72}$, has been isolated.

Spores and spore exines. - The reproductive organs of certain plants (in modern times only those of lower order) are known as spores and the water-proof casings associated with them are called exines. The presence of these plant substances in coal has been fully demonstrated by White and others;[29] the exines are especially well preserved, on account of their chemical inertness. Until very recently, the spores and spore exines in coal have interested the students of the origin and physical constitution of coal rather than the chemist. Now, however, in keeping with their broad research policy, British chemists are investigating these plant remains chemically with a view to determining their contribution to the chemical behavior of the coal conglomerate. While so far the work is unpublished, excellent progress is being reported.

IV. The Ulmins

The ulmin portion represents by far the most preponderant fraction of the coal conglomerate. The ulmins exist in nature in the soil, as so-called humins, in peat, lignite, and higher-ranking coals. They are generally regarded as derivatives of plant products and, according to the Fischer-Schrader theory of coal formation, are derived from the lignin portion of woody vegetation. The importance of the problem of determining the chemical constitution of ulmins is evident, for not only will its solution promote the intelligent utilization of coal, but it will also settle some important questions as to the origin of coal.

It is of course impossible within the scope of this paper to discuss at length the results of the enormous amount of work which has been done on ulmins. Fortunately, for the chemist, this is hardly necessary for it is only within the past decade that ulmin chemistry has emerged from the state of almost hopeless confusion of divergent opinions which characterizes the early development of any field of knowledge.

The introduction of the methods of modern physical and organic chemistry into the study of ulmins, especially by Oden, Fischer, Tropsch, Eller, Marcusson, and Fuchs, is beginning not only to illuminate the situation, but as usual is tending to simplify greatly the complex problem. This does not mean that even the fundamental points - such as, for example, the homogeneity of different ulmins - are all definitely established; but certainly the facts recently acquired allow a more consistent picture to be drawn and encourage the coal-research worker to feel that his goal is not hopelessly out of sight.

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Definition. - A satisfactory and universally accepted definition of the word "ulmin" does not exist. In this paper the work refers to all the substances or groups of substances regardless of origin or properties, which are variously referred to as humus, humins, humic acids, huminoids, and so forth. For the sake of further identification, they may be differentiated by the names soil ulmin, coal ulmin, synthetic ulmin, and the like. The word "ulmins" is used by the British, while the Germans and some Americans use "humins." The ulmins have been defined by Oden as those yellow-brown to dark black-brown substances of unknown constitution which are formed by the decomposition of organic matter.[30] Obviously, this is a broad definition and is open to criticism; Strache and Lant[31] have suggested a division of the field ulmins into five portions; but until our knowledge of the nature of ulmins is greater, it is hardly necessary to concentrate much effort on nomenclature. In the present discussion the ulmins will be considered collectively, and special reference will be made to similarities in the properties of the various substances.

Physical Properties. - The colloidal nature of ulmins is their most marked physical property. As this paper deals with their chemistry, it is sufficient to note that the ulmins have a great affinity for water, and when freshly prepared have a moisture content of 90 to 95 per cent. The colloidal nature of the ulmins creates many obstacles for the chemist who investigates them. For example, it is difficult to prepare a pure sample free from any adsorbed material. Indeed, there has been considerable controversy as to whether the nitrogen found in soil ulmins together with carbon, hydrogen, and oxygen is an inherent part of the ulmic substance or is extraneously adsorbed.

Chemical Properties: Composition. - The ulmins are compounds of carbon, oxygen, hydrogen, and possibly nitrogen. Analyses of different ulmic material show varying proportions of carbon from 58 to 68 per cent, hydrogen from 3 to 5 per cent, and sometimes a few per cent of nitrogen. These analyses lead to empirical formulas of approximately $C_5H_5O_2$ to $C_6H_4O_4$. Within this range lies the empirical formula $C_6H_4O_3$ which has often been advanced as the empirical formula of some ulmins. Francis and Wheeler[36] believe, however, that at least for coal ulmins the presence of nitrogen must be taken into account.

Molecular Weight and Formula. - The results of his extensive work lead Oden to conclude that the ulmins from sphagnum peat have a molecular weight of approximately 1350, as there are four acidic hydrogens; he suggested the formula $C_{60}H_{52}O_{24}(COOH)_4$. Fuchs and Leopold,[34, 35] in their work with three different ulmins - (1) Acidum Huminicum Merck, a commercial preparation from natural products; (2) a synthetic ulmic acid from starch; and (3) a synthetic acid from hydroquinone[36] - considered it likely that the approximate average molecular weight of these was 1400 and that they contained 3 to 4 replaceable hydrogen atoms. Further, more direct evidence is given by Fuchs,[37] who obtained from Kasseler brown coal ulmin an acetone-soluble nitrogen derivative having an average molecular weight of 1305. Francis and Wheeler[38] were unable to obtain any molecular weight values (they doubt if, owing to the colloidal nature of ulmins, this is possible), but found a value of 170 as against 350 found by Oden for the equivalent weight. From this they conclude that there is one hydroxyl and four carboxyls for each molecular unit of 680.

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Chemical Structure of Ulmins. - The publication of the Fischer-Schrader[17] theory of coal formation from the lignin portion of plants has given rise to a heated controversy over the chemical nature of coal, and hence of the ulmins which are its predominant constituent. The supporters of the theory, and they are in the majority, reasoned that the ulmins are phenolic - that is, aromatic in nature. The opponents, led by Marcusson,[39] insisted that the ulmins are derived from the non-aromatic cellulose and that ulmification has produced not aromatic six-membered all-carbon rings but five-membered furane rings containing four carbon and one oxygen atom. Others[40] have attempted to maintain a middle ground, and believe that neither theory is entirely correct. Thus a great deal has been written on the subject, and the matter is not closed by any means. However, it is unnecessary to recount in this paper the many pros and cons advanced by both sides, especially since they are not all free from speculation and inference. It seems advisable to withhold further opinion until more and better experimental evidence is at hand. The great value of the controversy is that it has stimulated workers to study the ulmins with increased interest and care, for it is realized that they hold the key to the solution, chemically at least, of the coal problem. It is certain that as the structure of lignin becomes known and as the process of ulmification is better understood, all of the apparently conflicting views which are based on facts will form one consistent picture.

Present Research. - At present the ulmin problem is being attacked from many directions. In Germany, Fuchs and his colleagues are studying the ulmins of brown coal. In the United States, the U. S. Bureau of Mines is carrying on work both on the ulmic portion of peat, and on the "regenerated" ulmins from bituminous coal. The problems are difficult and progress is comparatively slow; nevertheless the situation is far more hopeful than it was 10 years ago, and we may look hopefully to the future.

SUMMARY AND CONCLUSION

Recent accomplishments in the chemistry of coal have been outlined. Progress has been made mainly in (1) the study of the coal substance as a whole by microscopic means, treatment with solvents, attack by reagents, and decomposition by heat; (2) the more modern method of investigating separately the various constituents of coal such as the plant remains (cuticles and spore exines), resins, bitumens, and ulmins. Of these constituents, the ulmic portion is given the most attention because it is the most preponderant and doubtless most influences the properties of coal. Especial emphasis has been laid on the most recent work of Fuchs and of Francis and Wheeler. It is concluded that as a result of this work the coal research chemist can attack more hopefully the problem of the constitution of coal.

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